

Biodiesel Quality

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Outline

- ASTM specification
- Important quality parameters
- Storage stability
- BQ-9000
- Summary



What is biodiesel?

- Technical definition from the American Society for Testing and Materials (D 6751):

“Biodiesel consists of the alkyl monoesters of fatty acids derived from vegetable oils or animal fats.”



Liability

- The engine manufacturer/dealer is not responsible for problems caused by the fuel.
- The fuel supplier is liable for fuel-related problems.
- The fuel supplier might make \$5 to \$50 on a fuel sale, but he takes on liability for a \$10,000 to \$20,000 engine.
- Fuel quality is essential!

ASTM D 6751

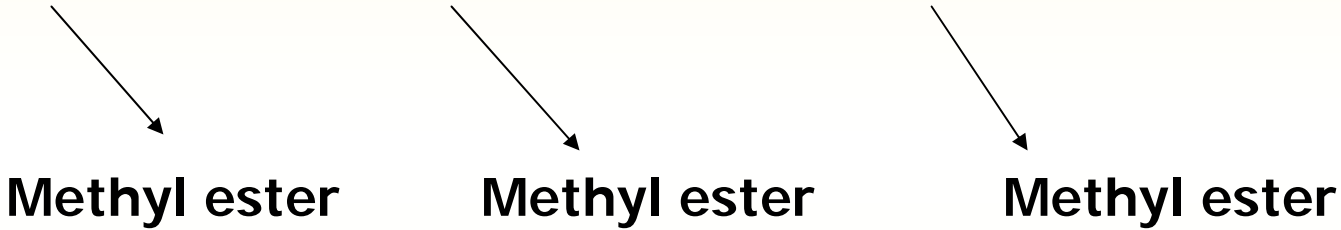
Property	Method	Limits	Units
Flash point, closed cup	D 93	130 min	° C
Water and sediment	D 2709	0.050 max	% volume
Kinematic viscosity, 40 ° C	D 445	1.9 – 6.0	mm ² /s
Sulfated ash	D 874	0.020 max	wt. %
Total Sulfur	D 5453	0.05 max for S500 0.0015 for S15	wt. %
Copper strip corrosion	D 130	No. 3 max	
Cetane number	D 613	47 min	
Cloud point	D 2500	Report to	° C
Carbon residue		<p>There is a specification for biodiesel that all producers should meet. Ask to see a Certificate of Analysis that proves the fuel meets the spec – or don't buy it!</p>	
Acid number			
Free glycerin			
Total glycerin			
Phosphorus			
Vacuum distillation end point			

Product Quality

- Product quality is important – modern diesel engines are very sensitive to fuel.
- It is not biodiesel until it meets ASTM D6751.
- Critical properties are total glycerol (completeness of reaction) and acid value (fuel deterioration). Reaction must be >98% complete.



Completeness of Reaction

- Triglyceride → Diglyceride → Monoglyceride → Glycerol


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graph LR; T[Triglyceride] --> D[Diglyceride]; D --> M1[Monoglyceride]; M1 --> G[Glycerol]; D --> ME1[Methyl ester]; M1 --> ME2[Methyl ester]; G --> ME3[Methyl ester];
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- Incomplete reaction mixtures contain tri-, di- and monoglycerides

Production issues

- Sum of the glycerin portion of the tri, di, and monoglycerides is called bound glycerin.
- Bound glycerin + free glycerin makes total glycerin.



What are the implications?

- If biodiesel doesn't meet the total glycerol specification, nothing else matters.
- High total glycerol can cause high viscosity.
- Tends to form white flakes or sediments at the bottom of tank. The main problem is saturated monoglycerides.
- May cause filter plugging.
- May contribute to deposit formation.

Causes of high total glycerol

- **Incomplete reaction. Getting a total glycerin below 0.24% requires 98% or better conversion of vegetable oil.**



How is it measured?

- Total glycerin is measured using a gas chromatograph (GC) (ASTM D6584).
- Outside laboratory testing costs \$80-150/test.
- A GC costs about \$40,000 and requires a trained operator. Realistically, all commercial producers need this capability on-site.
- AOCS method Ca 14-56 can be used as an alternative but can not be used to certify ASTM standard compliance.



Free glycerin

- Free glycerin is also a part of total glycerin and can be removed with a water wash.
- Warm water ($\sim 60^{\circ}\text{C}$) is more effective for water washing.
- Free glycerol also reduces the shelf life of biodiesel by absorbing atmospheric water and increasing water activity for microorganisms to grow.



Residual Alcohol

- European standards contain limits on alcohol (methanol) but the ASTM standard formally does not. It will soon.
- Flashpoint $> 130^{\circ}\text{C}$ will limit residual alcohol to less than 0.1%.
- Small amounts of alcohol will not affect engine.



Cloud point

- The temperature when wax crystal that is similar in appearance to a cloud is formed upon cooling at prescribed rate.
- Though there is no specification set by ASTM, it plays a major role in cold weather operability.
- Cloud Point and Pour Point have been routinely used to characterize the cold flow operability of diesel fuels.



Effect on biodiesel blend

- Each % of Soy biodiesel increases the pour point by 0.25°C whereas each % increase of canola or mustard biodiesel increases pour point by 0.1°C .



Storage Stability

- Chemical changes in fuel over time in presence of air.
- Catalyzed by higher temperature, some metals (container material!) and light.
- Unsaturated fatty acid chains form hydroperoxides, then aldehydes and short chain acids.
- If water is present, hydrolysis can occur and form long-chain fatty acids.

Storage Stability

- Acid value and viscosity increase with time and can be used as an indication that fuel has deteriorated.
- Currently no way to quantitatively determine the oxidation status of the biodiesel fuel that does not have significant disadvantages.
- Highly unsaturated fatty acids (C18:2, linoleic acid; C18:3 linolenic acid) oxidize more readily.



Storage Stability

- Additives such as BHT and TBHQ can enhance stability.
- Soybean and canola-based biodiesel has natural antioxidants (tocopherols, i.e., vitamin E).



BQ -9000 Quality Management Program

- Website: www.bq-9000.com
- Purpose: Ensure that quality fuel is marketed and used:
“The program is a unique combination of the ASTM standard for biodiesel, ASTM D 6751, and a quality systems program that includes storage, sampling, testing, blending, shipping, distribution, and fuel management practices.”
- Open to any biodiesel manufacturer, marketer or distributor of biodiesel and biodiesel blends in the United States and Canada.
- Like “Good Housekeeping Seal of Approval”



Testing requirements

- A COA must be generated for each production lot of fuel.
- Initially, full specification testing must be conducted on seven consecutive production lots. If successful, reduced testing is allowed.
- The following reduced set of tests must be conducted on every production lot:
 - Flash pt., water and sediment, cloud pt., Acid value, free and total glycerin, visual appearance.
- Full specification testing is required at least every 6 months.

Summary

- There is a specification for biodiesel.
- Quality is important for successful use of biodiesel.
- The key tests are: free and total glycerin, flash point, water and sediment, acid value, and visual appearance.
- Cloud point is not specified but must be reported.
- BQ-9000 ensures quality procedures are used.